(19) World Intellectual Property Organization International Bureau





(43) International Publication Date 4 September 2003 (04.09.2003)

PCT

(10) International Publication Number WO 03/073526 A2

(51) International Patent Classification7:

H01L 51/20

(21) International Application Number: PCT/GB03/00742

(22) International Filing Date: 20 February 2003 (20.02.2003)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

0204415.4

26 February 2002 (26.02.2002)

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- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHOD FOR PREPARING LIGHT EMITTING DEVICES

(57) Abstract: A process for preparing high efficiency light emitting devices and the devices prepared using this process are described. High efficiency light emitting devices may be prepared by providing a layer of porous low refractive index material, such as an aerogel, between the emitting layer of the device and the substrate. A method of preparing such light emitting devices comprising thermally patterning the layer of porous material of low refractive index is described. This method enables the preparation of high efficiency light emitting devices comprising porous low refractive materials using solution processing techniques.

Method for Preparing Light Emitting Devices

The present invention relates to a process for the preparation of substrates which are suitable for use in light emitting devices, to substrates prepared by this process and to light emitting devices, in particular electroluminescent devices, comprising such substrates.

Background of the invention

Light emitting devices include inorganic LEDs, thin film electroluminescent devices (TFELs), organic electroluminescent devices (OLEDs) which include both those devices in which the emissive centre comprises a polymer, such as are disclosed in WO90/13148 and, those devices in which the emissive centre comprises a small molecule, such as are disclosed in US4530507 and photoluminescent devices. A typical light emitting device comprises a layer of emissive material on a transparent substrate, light generated at the emissive centres passes through the transparent substrate into the surrounding air. In the case of an OLED or TFEL light is generated by applying a potential difference across the layer of emissive material, in the case of a photoluminescent device light is generated through incident light impinging on the film of emissive material.

A significant problem in the exploitation of light emitting devices is that much of the light generated in the emissive centres does not leave the device due to total internal reflection at both the interface between the high refractive index emitting material and the low refractive index transparent substrate and at the interface between the transparent substrate and the air, this phenomenon is shown schematically in Figure 1. Figure 1 shows an idealised light-emitting device 100, comprising a layer of light-emitting material 101 on a glass substrate 102, light is emitted from the emissive centres in all directions, rays with an internal emission angle greater than the critical angle are internally reflected and propagate within the emissive layer or the glass substrate. It has been estimated that in this way up to 80% of light generated at the emissive centres does not leave the device. Clearly the result of this is that much of the energy used to generate light does not result in light emission from the device, leading to light emitting devices having a low efficiency. In OLEDs this is expressed as the external

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electroluminescence quantum efficiency (the electron-to-photon conversion factor) being significantly lower than the internal quantum efficiency.

A number of attempts have been made to overcome this problem, principally by providing device architectures in which light is coupled out of the device. The use of microcavity structures in OLEDs has been shown to increase light output, Jordan et al Applied Physics Letters, 1996, 69, 1997. Layers of silica microspheres incorporated into OLEDs have been shown to increase light out-coupling by scattering waveguided light out of the emitting layer, Yamasaki et al Applied Physics Letters, 2000, 76, 1243. Light lost to waveguiding in the substrate has been effectively coupled out of OLEDs by providing spherically shaped patterns on the surface on the substrate, Madigan et al, Applied Physics Letters, 2000, 76, 1650.

More recently it has been shown that when a porous material having a very low refractive index, such as a thin silica aerogel layer, is positioned between the emitting layer and the substrate layer of an OLED an increase in light emission of a factor of 1.8 can be obtained, Tsutsui et al, Advanced Materials, 2001, 13, 1149 and EP1100129, such a device is shown in Figure 2. The electroluminescent device 200 comprises a glass substrate 201, a layer of silica aerogel 202, an anode comprising a layer of conducting indium-tin oxide 203, a layer of emitting material 204 and a metallic cathode 205. In the absence of the layer of silica aerogel light is trapped by internal reflection at the interface between the light emitting structure and the glass substrate. The silica aerogel, being of very low refractive index, serves to couple light out of the device, leading to a great improvement in device efficiency.

However a significant problem in the use of such porous materials of low refractive index in light emitting devices exists since many of the methods used to prepare light emitting devices require solution processing. During such solution processing steps liquid may enter the porous material and degrade its optical properties, for example by increasing its refractive index. In the case of OLEDs and TFEL devices it is generally necessary to deposit a patterned conducting material such as ITO onto the porous material, this is carried out using a photolithographic process which involves a developing solution. Depending on the nature of the eventual light emitting device other solution processing steps may be required, in particular recent progress in the development of polymer

based OLEDs relies extensively on solution processing techniques such as spin coating and ink-jet printing, as disclosed in WO98/24271.

The problem of liquid ingress into the porous layers of the above described devices is overcome by partially sealing the porous aerogel with a sputtered coating of silicon dioxide. Although this sealing method is sufficient to prepare a single light emitting device on a single, isolated substrate current manufacturing techniques for preparing light emitting devices require a number of devices to be prepared on a single substrate with this substrate being divided at a later stage in the manufacturing process to provide a number of separate devices. The scribing of the devices from the single substrate layer leaves the porous aerogel exposed allowing liquid to enter the pores during further processing of the device, or if the device is cut from the substrate following encapsulation the porous aerogel is exposed to ambient moisture around the edges of the device, this moisture may enter the aerogel, degrading the performance of the device and requiring a further encapsulation step to prevent ingress of ambient moisture into the aerogel layer.

There exists a problem to provide an efficient light-emitting device and in particular a method of producing such a device which can be readily incorporated into current manufacturing methods such as those methods wherein a plurality of light-emitting devices are prepared on a single substrate using steps involving solution processing.

Summary of the invention

The present inventors have found that by treating a layer of porous material of low refractive index on a substrate with a heat source the porous material can be made to melt and its porous structure to collapse, forming a non-porous structure into which fluid cannot enter thereby effectively sealing the porous material of low refractive index and preventing the ingress of fluid. Further the present inventors have found that by treating selected areas of the layer of porous material of low refractive index with a heat source said layer can be patterned, for example to define a two-dimensional array of light-emitting devices. The heating of selected areas using a heat source is herein referred to as thermal patterning, wherein the layer of porous material of low refractive index is

patterned into non-porous heat treated regions into which ingress of fluid is not possible and non-heat treated regions which remain porous.

This finding has been applied to the preparation of light-emitting devices providing a process for the preparation of efficient light-emitting devices which enables porous materials of low refractive index to be used in manufacturing processes which involve solution processing steps.

In a first embodiment the present invention provides a process for the preparation of a substrate suitable for use in light emitting devices comprising the steps of providing a transparent substrate, providing a layer of porous material of low refractive index on said substrate and sealing said layer of porous material of low refractive index to prevent the ingress of fluid, characterised in that said process further comprises a step of thermally patterning said layer of porous material of low refractive index

In a further embodiment the thermal patterning of said layer of porous material of low refractive index may be carried out prior to said step of sealing said layer of porous material of low refractive index or following said step of sealing said layer of porous material of low refractive index.

In a further embodiment the step of sealing said layer of porous material of low refractive index comprises providing a layer of non-porous material over said layer of porous material of low refractive index. The non-porous material may be a oxide such as silicon dioxide and may be applied by any suitable process such as sputtering, thermal evaporation or vacuum deposition. Prior to said step of sealing the porous layer of low refractive index this layer may be treated with a hydrophobising agent, such as an alkylsilane or alkylsilazine.

In a further embodiment the step of thermally patterning said layer of porous material of low refractive index comprises treating selected regions of said layer of porous material of low refractive index with a heat source selected from the group comprising lasers, heated probes and heated wires. Preferably said step of thermally patterning said layer of porous material of low refractive index comprises treating selected regions of said layer of porous material of low refractive index with a laser selected from the group

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comprising laser diodes, gas lasers and solid state lasers. Preferably said laser is an infrared laser such as a CO_2 laser.

In a preferred embodiment the refractive index of said porous material of low refractive index is from 1 to 1.3, more preferably 1.01 to 1.2. Any suitable porous material of low refractive index may be used in the present invention but preferably said porous material of low refractive index is an aerogel, more preferably an aerogel selected from the group comprising melamine-formaldehyde aerogels, polymethylmethacrylate aerogels, phenol-formaldehyde aerogels, polyisocyanate aerogels and silica aerogels. Preferably said porous material of low refractive index is a silica aerogel.

In a further embodiment of the process of the present invention said transparent substrate is selected from the group comprising glass, acrylic resins, polycarbonate resins, polyester resins, polyethylene terephthalate resins and cyclic olefin resins.

Other embodiments of the present invention are directed to the further steps involved in the preparation of light-emitting devices on the substrates of the present invention. One embodiment comprises the step of providing a layer of conductive material over said layer of porous material of low refractive index, in a further embodiment this layer of conductive material is patterned using solution processing. Said conductive material is preferably selected from the group comprising indium-tin oxide, tin oxide, aluminum or indium doped zinc oxide, magnesium-indium oxide, cadmium tin-oxide, Au, Ag, Ni, Pd and Pt. Most preferably said conductive material is indium-tin oxide (ITO).

The present invention is also directed to a substrate obtainable by the process of the present invention, a light emitting device obtainable by the process of the present invention, where preferably said light-emitting device is an electroluminescent device, more preferably said electroluminescent device comprises a solution processable semiconductive polymer.

Brief description of figures

Figure 1 illustrates how light generated at the emissive centres of a light-emitting device does not leave the device due to internal reflection and waveguiding.

Figure 2 shows a prior art electroluminescent device with a layer of silica aerogel.

Figure 3 shows a plurality of light emitting devices in a two dimensional array on a substrate.

Figure 4 illustrates the manufacturing of several electroluminescent devices on a single substrate in a process where thermal patterning is not used.

Figure 5 illustrates the manufacturing of several electroluminescent devices on a single substrate according to the present invention.

Figure 6 shows an electroluminescent device according to the present invention comprising a solution processable semiconductive polymer.

Detailed description of a preferred embodiment

The above referenced work of Tsutsui et al has shown how increased light emission can be obtained from light-emitting devices and in particular organic electroluminescent devices through the positioning of a layer of a porous, low refractive index material such as a silica aerogel between the emitting layer and the substrate of such devices. It has been demonstrated that this layer of low refractive index acts to couple light out of the device, a doubling of coupling-out efficiency has been observed in these devices.

Tsutsui et al demonstrate the effect of the layer of porous material of low refractive index using a silica aerogel such as those disclosed in US5830387, US5496527, JP5279011, US5124364, US5137927, US4402927, US4432956 and US4610863, other suitable porous materials of low refractive index may also be used, for example the polyisocyanate aerogels disclosed in WO00/32663, phenol-formaldehyde aerogels of US5744510 and US4997804 and the melamine-formaldehyde aerogels of US5086085.

As discussed above although the method of preparing a device of Tsutsui et al provides devices of greatly improved efficiency, many of the steps currently used to prepare light-emitting devices involve solution processing and during such solution processing ingress of solvent into the porous material is likely to occur and this will degrade the porous

material, for example by increasing its refractive index. In particular current light-emitting device manufacture generally involves the preparation of a plurality of light-emitting devices in the form of a two dimensional array on a single substrate which is then scribed to give the individual light-emitting devices. Figure 3 illustrates a substrate 301 with a two dimensional array of devices 302. A substrate may be of size 350 mm² and individual devices of size 20 mm by 30 mm, clearly the size of device and substrate will depend on the intended use of the device.

An example of a process in which a substrate comprising a plurality of electroluminescent devices having a layer of porous material of low refractive index is prepared is illustrated in Figure 4. A layer of silica aerogel 402 is deposited upon a glass substrate 401 using a sol-gel process, after gelation and ageing the gel may be treated with a hydrophobising agent such a hexamethyldisilazane, the aerogel is then supercritically dried, for example by heating at 80 °C in an autoclave in a CO2 atmosphere at a pressure of 16 MPa, such techniques for preparing aerogels are well known in the art. The aerogel coated substrate is then sealed with a layer of SiO₂ 403 to prevent the ingress of fluid into the porous silica aerogel. The SiO₂ may be deposited by sputtering in such a manner that it not only seals the surface of the silica aerogel layer but also the edges of the silica aerogel which are exposed around the edge of the substrate. The aerogel coated substrate then has a layer of conductive material such indium-tin oxide 404 deposited upon it by sputtering. This conductive layer is then patterned using photolithography, wherein the layer of indium-tin oxide is coated with a photoresist, patterned, for example using a UV source and a photomask, and developed using the appropriate developing solution, exposed indium-tin oxide is then removed by chemical etching, leaving a patterned layer of ITO 405.

A layer of light-emitting material **406** such as aluminum trisquinoline or polyphenylene is then deposited, other layers such as charge-transporting layers may also be deposited. Generally where the emitting material or charge transporting material is a polymer these are deposited using solution processing such as spin coating, to deposit a layer of polymer over the entire substrate, or ink-jet printing, to deposit polymer in selected areas of the substrate. A patterned cathode **407** is then deposited, for example by sputtering or vapour deposition. Typically the individual devices are then encapsulated using a metal can **408**, and then scribed from the

substrate and connected to external drive circuitry. The cutting of the encapsulated devices exposes the silica aerogel to the atmosphere, shown at arrows 409, and allows moisture to enter the porous structure of the aerogel and degrade its performance. In order to avoid this it is necessary to carry out a further sealing or encapsulation step around the edges of the device so as to seal the aerogel.

In the above described process the substrate is not sub-divided until after encapsulation of the device. If it is necessary to cut the substrate prior to encapsulation it is of even greater importance to seal the porous aerogel since as indicated above a number of the processing steps involve solution processing, the solutions used in these processing steps may enter into the pores of the aerogel and so degrade its performance. It is an object of the present invention to provide a process for preparing light-emitting devices which allows the use of both porous materials of low refractive index and solution processing without the disadvantages of the process outlined above.

Preferred methods for preparing substrates according to the present invention are now described and illustrated in Figure 5. A transparent substrate 501 coated with a layer of porous material of low refractive index 502 is prepared. Since the porous materials of low refractive index considered in the present invention are generally prepared by means of a gel precursor this can involve preparing the porous material in situ on the substrate with the porous material thereby forming a layer conforming to the surface of the substrate and in intimate contact with said surface as is exemplified in EP1100129. Other methods of preparation may be envisaged such as whereby a preformed layer of porous material is deposited upon the substrate or granules of porous material are deposited upon the substrate then treated to form a monolithic layer of porous material. The substrate may be a rigid material such a glass or rigid plastic or a flexible material such as an acrylic resin, a polycarbonate resin, a polyester resin, a polyethylene terephthalate resin or a cyclic olefin resin. Where it is intended that the eventual lightemitting device is flexible a suitable porous material must be selected, such as one of the organic polymer based aerogels referred to above.

The porous material on the coated substrate is then sealed **503**, for example by sputtering a layer of silicon dioxide onto its surface, the substrate is then thermally patterned to define the individual light-emitting devices **504**. Alternatively the substrate

may be first thermally patterned to define the individual light-emitting devices **506** and then sealed **507**. The latter process is preferred as it allows the silicon dioxide and any further layers of material which are deposited by sputtering to be deposited in the same vacuum chamber.

Thermal patterning may be carried out by moving a point heat source across the surface of the porous material such that the temperature of the porous material in the region to which the heat source is applied rises sufficiently to melt the porous material, causing its porous structure to collapse rendering that region non-porous. Alternatively a patterned heat source may be used. The heat source may be a heated probe such as a metal wire or point but is preferably a laser since lasers offer a greater degree of directional control, the laser source can be matched to the optical absorption characteristics of the porous material being used and the use of lasers avoids any contamination of the substrate. Examples of laser include gas lasers such as CO₂, CO, solid state lasers such as Nd:YAG, Nd:glass, Er:YAG, Ho:YAG, Nd:YLF, Cr:Th:Ho:YAG and laser diodes. Preferred lasers are CO₂ lasers emitting in the infrared at 10.6 microns. One particular method of heating which provides a high degree of precision involves heating the entire substrate to a temperature slightly below the melting point of the porous material using conventional means, such as a hot plate and then applying a laser heat source to the regions to be patterned to cause the temperature in these regions to rise above the melting point of the porous material. In practice the laser is supported above the coated substrate and the substrate is translated in both X and Y directions. Alternatively the substrate is translated in one direction and the laser is scanned in the other or the laser may be scanned in both X and Y directions. In this way patterned regions of melted and non-melted porous material may be defined. The substrate is generally patterned to define a two dimensional array of the eventual light-emitting devices, a typically patterned substrate is shown in Figure 3. The thermally patterned porous material coated substrate may then be processed using solution processing techniques to provide an efficient light-emitting device without the risk of the processing solutions used ingressing into the porous material and degrading its properties.

The application of the present invention is now described in detail for the preparation of electroluminescent devices on the substrates of the present invention. It would be

obvious to a person skilled in the art as to how this teaching could be applied to the preparation of other types of light-emitting devices such as photoluminescent devices.

A transparent conducting electrode is provided on the surface of the thermally patterned substrate by depositing a transparent conducting material such as indium-tin oxide (ITO) on the thermally patterned substrate by sputtering, other transparent conducting materials such tin oxide (TO), aluminum or indium doped zinc oxide, magnesium-indium oxide, cadmium tin-oxide and metals such as Au, Ag, Ni, Pd and Pt may also be used. The ITO is then patterned using a photolithographic process as is well known in the art whereby the ITO is coated with a photoresist, exposed to a source of ultraviolet light through a photomask and developed using an appropriate developing solution. It is noted that the steps of coating the ITO with a photoresist and developing the patterned ITO both involve solution processing, the thermally patterned substrates of the present invention prevent these solutions degrading the porous material on the substrate.

A layer of hole-transporting material is then deposited upon the patterned ITO, the preferred hole-transport material used in the art is a polystyrene sulfonic acid doped polyethylene dioxythiophene (PEDOT:PSS) as disclosed in WO98/05187, although other hole transporting materials such as polyaniline or TPD (N,N'-diphenyl-N,N'-bis(3methylphenyl)[1,1'-biphenyl]-4,4'-diamine) may also be used. PEDOT:PSS is deposited by solution processing techniques such as spin-coating, doctor-blade coating or printing, such as screen-printing or ink-jet printing. A layer of light-emitting polymer such as a polyfluorene or a polyphenylene vinylene, is then deposited upon the layer of holetransporting material, solution processing techniques are the preferred methods for depositing such light-emitting polymers, in particular spin coating or ink-jet printing. In the case of an electroluminescent device comprising small molecule charge transporters and light-emitters these may be deposited by vapour deposition or by solution processing. Examples of polymeric light emitting materials and charge transporting materials can be found in Bernius et al Advanced Materials, 2000, 12, 1737, examples of small molecule light emitting materials and charge transporting materials can be found in US5294869.

Following deposition of the emitting material a cathode is deposited. Examples of suitable materials for the cathode include Li, Na, K, Rb, Be, Mg, Ca, Sr, Ba, Yb, Sm and

Al. The cathode may comprise an alloy of such metals or an alloy of such metals in combination with other metals, for example the alloys MgAg and LiAl. The cathode preferably comprises multiple layers, for example Ca/Al or LiAl/Al. The device may further comprise a layer of dielectric material between the cathode and the emitting layer, such as is disclosed in WO 97/42666. In particular it is preferred to use an alkali or alkaline earth metal fluoride as a dielectric layer between the cathode and the emitting material. A particularly preferred cathode comprises LiF/Ca/Al, with a layer of LiF of thickness from 1 to 10nm, a layer of Ca of thickness of 1 to 25nm and a layer of Al of thickness 10 to 500nm. A particularly preferred cathode has the structure BaF₂/Ca/Al.

The devices obtained may be further processed, for example to provide electrical connectors to connect the electrodes of the devices to eventual driver electronics. The devices are then encapsulated and cut from the substrate, alternatively the devices are first cut from the substrate and then encapsulated. Encapsulation may be carried out by means of enclosing the device in a metal can or glass cover to protect the device from the environment, an oxygen or moisture absorbent may be including within the metal can or glass cover, such a technique is disclosed in US6080031. Alternatively devices may be encapsulated by laminating an impermeable composite material over the device as is disclosed in WO00/36661. A number of the above described steps used in preparing a two dimensional array of polymer light-emitting devices on a single substrate are further described in WO01/39287.

Figure 6 shows a light-emitting device 600 prepared according to the present invention after being scribed and separated from the rest of the substrate. The device comprises a transparent substrate 601, such as glass, a layer of porous material of low refractive index 602, such as a silica aerogel, a layer of material serving to seal said porous material 603, the sealing layer may be a layer of sputter deposited SiO₂, an anode, for example ITO, 604, a layer of light emitting material, such as a polyfluorene, 605, a metallic cathode 606 a connector 607 enabling the cathode to be connected to a driver and an encapsulating metal can 608. It can be seen that the thermal patterning serves to prevent the ingress of atmospheric moisture into the device at points 609 which would otherwise occur.

It is noted that at no point during these later processing steps is the porous material exposed to the atmosphere or to any processing solutions. The optical properties of the porous material are not then degraded by the ingress of liquid into the pores of the material and the porous material of low refractive index retains its ability to couple light out of the light-emitting device increasing the efficiency of the device.

No doubt the teaching herein makes many other embodiments of, and effective alternatives to, the present invention apparent to a person skilled in the art. The present invention is not limited to the specific embodiments described herein but encompasses modifications which would be apparent to those skilled in the art and lying with the spirit and scope of the attached claims.

Claims

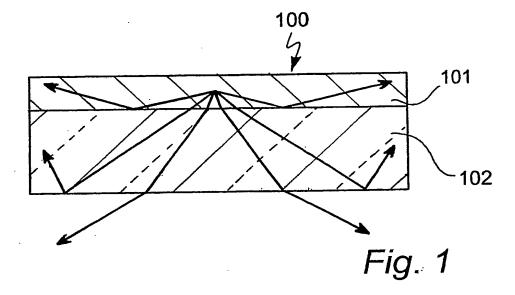
1. A process for the preparation of a substrate suitable for use in light emitting devices comprising the steps of providing a transparent substrate, providing a layer of porous material of low refractive index on said substrate and sealing said layer of porous material of low refractive index to prevent the ingress of fluid, characterised in that said process further comprises a step of thermally patterning said layer of porous material of low refractive index.

- 2. Process according to claim 1 wherein said step of thermally patterning said layer of porous material of low refractive index is carried out prior to said step of sealing said layer of porous material of low refractive index.
- 3. Process according to claim 1 wherein said step of thermally patterning said layer of porous material of low refractive index is carried out following said step of sealing said layer of porous material of low refractive index.
- 4. Process according to claim 1 wherein said step of sealing said layer of porous material of low refractive index comprises providing a layer of non-porous material over said layer of porous material of low refractive index.
- 5. Process according to claim 4 wherein said step of providing a layer of non-porous material over said layer of porous material of low refractive index comprises applying a layer of silicon dioxide by sputtering, thermal evaporation or vacuum deposition.
- 6. Process according to claim 1 further comprising the step of treating said layer of porous material of low refractive index with a hydrophobising agent prior to said step of sealing said layer of porous material of low refractive index.
- 7. Process according to claim 1 wherein said step of thermally patterning said layer of porous material of low refractive index comprises treating selected regions of said layer of porous material of low refractive index with a heat source selected from the group comprising lasers, heated probes and heated wires.

8. Process according to claim 7 wherein said step of thermally patterning said layer of porous material of low refractive index comprises treating selected regions of said layer of porous material of low refractive index with a laser selected from the group comprising laser diodes, gas lasers and solid state lasers.

- 9. Process according to claim 1 wherein the refractive index of said porous material of low refractive index is from 1 to 1.3.
- 10. Process according to claim 9 wherein the refractive index of said porous material of low refractive index is from 1.01 to 1.2.
- 11. Process according to claim 1 wherein said porous material of low refractive index is selected from the group comprising melamine-formaldehyde aerogels, polymethylmethacrylate aerogels, phenol-formaldehyde aerogels, polyisocyanate aerogels and silica aerogels.
- 12. Process according to claim 11 wherein said porous material of low refractive index is a silica aerogel.
- 13. Process according to claim 1 wherein said transparent substrate is selected from the group comprising glass, acrylic resins, polycarbonate resins, polyester resins, polyethylene terephthalate resins and cyclic olefin resins.
- 14. Process according to claim 1 further comprising the step of providing a layer of conducting material over said layer of porous material of low refractive index.
- 15. Process according to claim 14 further comprising the step of patterning said layer of conducting material using solution processing.
- 16. Process according to claim 14 wherein said conducting material is selected from the group comprising indium-tin oxide, tin oxide, aluminum or indium doped zinc oxide, magnesium-indium oxide, cadmium tin-oxide, Au, Ag, Ni, Pd and Pt.

- 17. Substrate obtainable by the process of any of claims 1 to 16.
- 18. Light emitting device obtainable by the process of any of claims 1 to 16.
- 19. Electroluminescent device obtainable by the process of any of claims 1 to 16.
- 20. Electroluminescent device comprising a solution processable polymer obtainable by the process of any of claims 1 to 16.
- 21. A method of preparing an electroluminescent device comprising the process of any of claims 1 to 16.



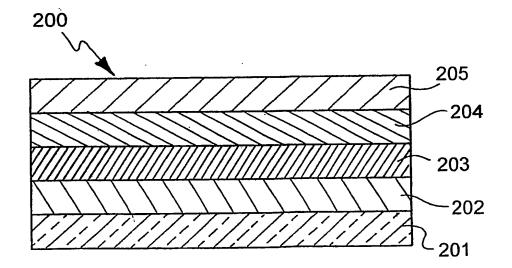


Fig. 2

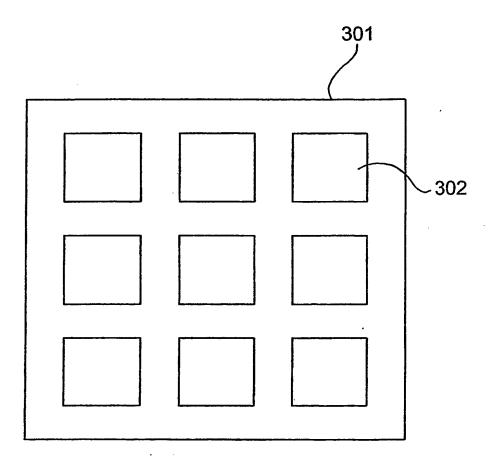
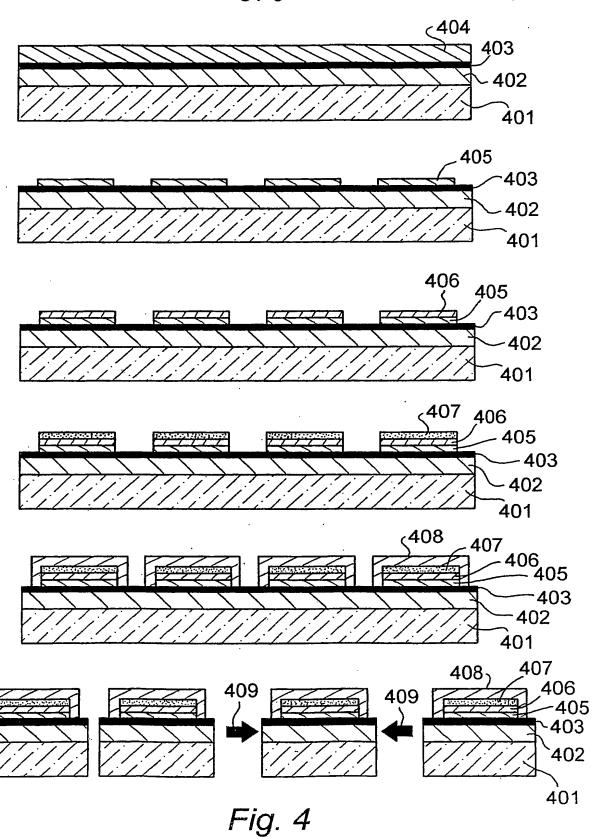


Fig. 3

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4/5

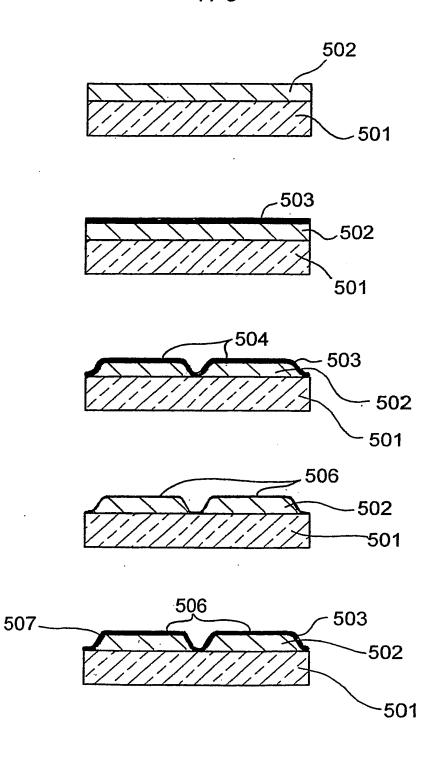


Fig. 5

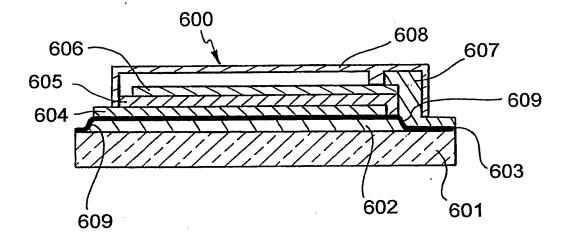


Fig. 6

(19) World Intellectual Property Organization International Bureau



(43) International Publication Date 4 September 2003 (04.09.2003)

PCT

(10) International Publication Number WO 03/073526 A3

(51) International Patent Classification7:

H01L 51/20

- (21) International Application Number: PCT/GB03/00742
- (22) International Filing Date: 20 February 2003 (20.02.2003)
- (25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

0204415.4

26 February 2002 (26.02.2002) GI

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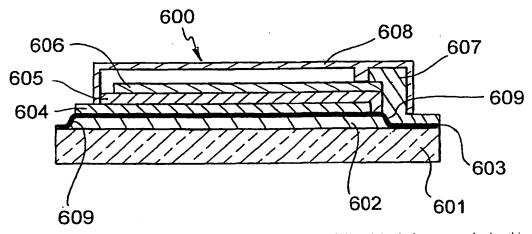
- (74) Agent: SHADE, Matthew; Representative Registration No. 45072, Cambridge Display Technology Limited, Greenwich House, Madingley Road, Madingley Rise, Cambridge, Cambridgeshire CB3 0TX (GB).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
- (88) Date of publication of the international search report:

[Continued on next page]

(54) Title: METHOD FOR PREPARING LIGHT EMITTING DEVICES



(57) Abstract: A process for preparing high efficiency light emitting devices (600) and the devices prepared using this process are described. High efficiency light emitting devices may be prepared by providing a layer of porous low refractive index material (602), such as an aerogel, between the emitting layer (605) of the device and the substrate (601). A method of preparing such light emitting devices comprising thermally patterning the layer of porous material of low refractive index is described. This method enables the preparation of high efficiency light emitting devices comprising porous low refractive materials using solution processing techniques.

03/073526 A3

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Internal pplication No PCT/GB 03/00742

A. CLASSIF IPC 7	ICATION OF SUBJECT MATTER H01L51/20			
According to	International Patent Classification (IPC) or to both national classification	on and IPC		
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Minimum doo	cumentation searched (classification system followed by classification H01L H05B	symbols)		
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Documentati	on searched other than minimum documentation to the extent that suc	ch documents are included in the helds see	ucieu	
Electronic da	ala base consulted during the international search (name of data base	and, where practical, search terms used)		
	ternal, INSPEC, PAJ, WPI Data			
C. DOCUME	ENTS CONSIDERED TO BE RELEVANT			
Category °	Citation of document, with indication, where appropriate, of the relevant	vant passages	Relevant to claim No.	
A	TSUTSUI T ET AL: "DOUBLING COUPL EFFICIENCY IN ORGANIC LIGHT-EMITT DEVICES USING A THIN SILICA AEROG ADVANCED MATERIALS, VCH	1,4-6, 9-14, 16-19,21		
A	VERLAGSGESELLSCHAFT, WEINHEIM, DE vol. 13, no. 15, 3 August 2001 (2001-08-03), pages 1149-1152, XP001129642 ISSN: 0935-9648 cited in the application the whole document EP 1 100 129 A (MATSUSHITA ELECTR LTD;TSUTSUI TETSUO (JP)) 16 May 2001 (2001-05-16)		1,6, 9-14, 16-19,21	
	cited in the application page 7, column 11, paragraph 48 - column 17, paragraph 76	-/		
X Fur	ther documents are listed in the continuation of box C.	χ Patent family members are listed	in annex.	
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Name and	d mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (-31-70) 340-3016	Authorized officer De Laere, A		

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Internat I Application No
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	ation) DOCUMENTS CONSIDERED TO BE RELEVANT	Deliver No.		
Category °	Citation of document, with Indication, where appropriate, of the relevant passages	Relevant to claim No.		
A	HRUBESH L W ET AL: "Thin aerogel films for optical, thermal, acoustic and electronic applications" JOURNAL OF NON-CRYSTALLINE SOLIDS, NORTH-HOLLAND PHYSICS PUBLISHING. AMSTERDAM, NL, vol. 188, no. 1-2, 1 July 1995 (1995-07-01), pages 46-53, XP004067975 ISSN: 0022-3093 page 49, column 1, paragraph 2.7	1,4, 9-15,17		
Α	WO 01 82390 A (EMAGIN CORP) 1 November 2001 (2001-11-01) page 7, line 2 -page 11, line 2	1		
	·			

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

nation on patent family members

Internation Application No
PCT/GB 03/00742

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
EP 1100129	A	16-05-2001	JP JP CN EP	2001202827 A 2001266768 A 1296295 A 1100129 A2	27-07-2001 28-09-2001 23-05-2001 16-05-2001
WO 0182390	A	01-11-2001	US AU WO US WO	2001052752 A1 5519401 A 0182390 A1 2002003403 A1 02071506 A1	20-12-2001 07-11-2001 01-11-2001 10-01-2002 12-09-2002

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